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The TiO-band 11032 A

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With 1 figure in the text

ABSTRACT

A rotational analysis of the infrared TiO-band 11032.2 A has been carried out. It is the 0-0 band of a $^1\Pi$–$^1\Sigma$ transition, which has the upper state in common with the $^1\Pi$–$^1\Delta$-band at 8860 A.

Introduction

Two singlet band systems have so far been identified in the spectrum of the TiO-molecule, both analyzed by Phillips [1]. An infrared band system at 8860 A corresponds to a $^1\Pi$–$^1\Delta$ transition, and a yellow one at 5598 A to a $^1\Phi$–$^1\Delta$. They have the lower state in common. Two triplet systems have been identified in the TiO-band spectrum, but they are not relevant to this case.

The 11032 A-band now analyzed was reported by Wurm and Meister [2] in 1937. They found a large number of band heads in the region 8000 A to 11238 A.

Experimental

The 11032 A-band was photographed on sensitized Kodak I-Z(2) plates in a first order of a Wood's 21 ft. concave grating (165 000 lines in all). The source of light was an arc burning between titanium rods 3 mm in diameter. It was run at a current of 2 to 3 A from a 440V D.C. supply. The lower, negative electrode was consumed and had to be renewed, whereas the upper, positive electrode, being of lesser importance, could be used even after being burned up to the copper holder. The band-spectrum was exposed for 2 hours through a Corning filter 2-64. The slit width was 0.15 mm. Iron lines were used for comparison.

The structure of the band

The appearance of the band is shown in fig. 1. It is degraded to longer wavelengths. There are three branches, one *R*, one *P*, and one *Q* branch. The *Q*-branch is intense, which indicates $\Delta\Lambda = \pm 1$.

The rotational structure is almost completely resolved in the vicinity of the origin, but the first *P*-lines are too weak to be detected among the *Q* and *R* lines.

The band is blended by several weaker bands, which makes it impossible to study the isotope effect.

No perturbations were found. The presence of overlapping bands, however, makes it difficult to be sure that these are absent.

Table 1. Wave-numbers of the 11032 A-band.

J	*R*	*Q*	*P*	*J*	*R*	*Q*	*P*
0	9055.01	—	—	40	9037.25	8995.74	8954.70
1	55.95	9054.12	—	41	35.34	92.84	50.81
2	56.86	53.84		42	33.37	89.84	46.78
3	57.68	53.59*		43	31.25	86.77	42.65
4	58.43	53.30		44	29.10*	83.64*	38.50
5	59.01	52.92		45	26.94	80.47	
6	59.70	52.48*	9046.11	46	24.64	77.17	29.95
7	60.21	52.05	44.81	47	22.32	73.83	25.66
8	60.63	51.49	43.15*	48	19.92	70.42	21.21
9	61.01	50.82	41.56	49	17.42	66.93	16.71
10		50.05*	39.91	50	14.86	63.37	12.13
11		49.32	38.07	51	12.19	59.75	
12		48.48	36.05*	52	09.51	56.02	
13		47.54		53	06.69*	52.28*	8897.96
14		46.54	32.18	54	03.82	48.56	
15		45.49	30.07	55	00.95	44.54	
16		44.39	27.93	56	8997.92	40.55	
17	61.55	43.15*	25.69	57	94.86	36.46	
18	61.26	41.84	23.47	58	91.71	32.29	
19	60.89	40.49		59	88.48	28.14	
20	60.49	39.11*		60	85.22	23.87	
21	60.02	37.59	16.10	61	81.82	19.55	
22	59.46	36.05*	13.46	62	78.41	15.16	
23	58.82	34.40	10.78	63	74.88	10.68	
24	58.15	32.69	08.08	64	71.31	06.10	
25	57.41	30.92	05.30	65	67.64	01.52[a]	
26	56.56	29.10*	02.42	66	63.90	8896.78	
27	55.63	27.14	8999.46	67	60.13	91.97	
28	54.63	25.15	96.45	68		87.19	
29	53.59*	23.08	93.36	69	52.28*	82.39	
30	52.48*	20.98	90.15	70	48.27		
31	51.28	18.78	86.99	71	44.21		
32	50.05*	16.49	83.64*	72	40.08		
33	48.68	14.16		73	35.81		
34	47.26	11.72	76.85	74	31.50		
35	45.77	09.22	73.35	75	27.07		
36	44.21	06.69*	69.78	76	22.67		
37	42.57	04.09	66.13	77	18.15		
38	40.87	01.36	62.34	78	13.51		
39	39.11*	8998.58	58.54	79	08.86		
				80			
				81	8899.39		

* overlapped by another rotational line.

[a] overlapped by atomic line.

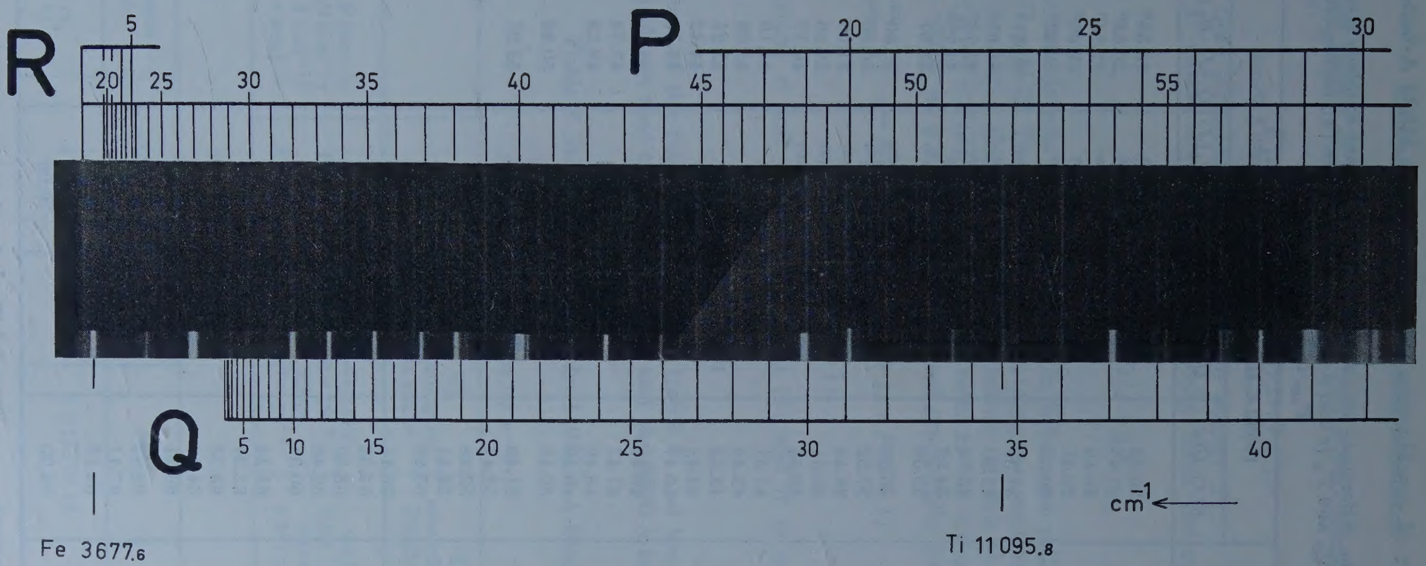

Fig. 1. Reproduction of the 11032.2 A-band of TiO, photographed on sensitized Kodak I-Z(2) plates with a Wood's 21 ft. concave grating (165 000 lines in all). Iron lines (3rd order) from an ordinary arc are used for comparison.

Table 2. Comparison of combination differences of the 11032 A-band and the 8860 A-band.

For the 8860 A-band the differences are calculated from the wave-numbers given by Phillips [1]. The designations R_d, Q_c, and P_d (c and d according to Mulliken [3]) correspond to R_{ab}, Q_b, and P_{ab}, in Phillips paper.

J	11032 A-Band		8860 A-Band	
	$R(J)-Q(J)$	$Q(J)-P(J)$	$R_d(J)-Q_c(J)$	$Q_c(J)-P_d(J)$
25	26.49	25.62	26.57^{n}	25.58^{n}
26	27.45	26.69	27.61^{n}	26.63^{n}
27	28.49	27.68	28.58^{n}	27.74^{n}
28	29.47	28.70	29.59^{n}	28.60^{n}
29	30.51	29.72	30.69^{n}	29.62^{n}
30	31.50	30.84	31.66^{n}	30.61^{n}
31	32.50	31.79	32.67^{n}	31.67^{n}
32	33.56	32.86	33.63^{n}	32.76^{n}
33	34.52		34.71^{n}	33.72^{n}
34	35.54	34.87	35.52$^{(n)}$	34.97
35	36.55	35.87	36.65$^{(n)}$	35.80$^{(n)}$
36	37.52	36.91	37.54$^{(n)}$	36.80$^{(n)}$
37	38.49	37.96	38.56$^{(n)}$	37.98
38	39.51	39.02	39.56$^{(n)}$	38.86
39	40.53		40.68$^{(n)}$	40.17
40	41.51	41.04	41.50	41.10
41	42.49	42.03	42.56	42.09
42	43.53	43.06	43.49	43.21
43	44.48	44.12	44.51	44.12
44	45.47	45.14	45.53	45.16
45	46.47		46.60	46.19
46	47.47	47.22	47.55	47.14
47	48.49		48.50	48.23
48	49.50			
49	50.49		50.48	50.25
50	51.49	51.24	51.54	51.27
51	52.44		52.51	
52	53.48		53.41	
53	54.41		54.44	
54	55.26		55.41	
55	56.41		56.38	
56	57.38		57.35	
57	58.39		58.38	
58	59.43		59.37	
59	60.34		60.35	
60	61.34		61.27	
61	62.27		62.32	
62	63.25		63.26	
63	64.20		64.29	
64	65.21		65.23	
65	66.13		66.21	
66	67.11		67.13	
67	68.15		68.15	
68			69.16	
69	69.90		70.05	

[1] Λ doublets not resolved.

$^{(n)}$ one of the Λ doublets not resolved.

Evaluation of the rotational constants

The rotational energy of a $^1\Sigma$-term or one of the two components of a $^1\Pi$-term may be written:

$$F(J) = BJ(J+1) - DJ^2(J+1)^2.$$

$(A-B)\Lambda^2$ is here included in the electronic energy T_e.
The B and D values are obtained graphically from the equation

$$\frac{\Delta_2 F(J)}{J+\frac{1}{2}} = 4B - 8D(J+\tfrac{1}{2})^2.$$

The combination defects in the combination differences (table 2) show that the transition is Σ–Π or Π–Σ. The R-branch is very strong as compared with the P-branch, which makes the latter alternative more probable. If this is so, then the equation $\Delta_2 F'(J) = R(J) - P(J)$ will in this band refer to the lower components of the $^1\Pi$-terms. The value of $q = B_c' - B_d'$ is obtained graphically from the formulas

$$\varepsilon = R(J) - Q(J) - Q(J+1) + P(J+1)$$

and

$$\tfrac{1}{2}\varepsilon = qJ(J+1).$$

The designations c and d follow Mulliken [3] and it is assumed that the Σ is a Σ^+.

Discussion

The agreement of the rotational constants (table 3) and the combination differences (table 2) shows that the 11032 A-band and the 8860 A-band have the upper

Table 3. Band-constants of the 11032.2 A-band.

$\nu_0 = 9054.00$ cm^{-1}.

B, D, q, and r values for $v = 0$:

	$^1\Sigma$	$^1\Pi$ according to this paper	$^1\Pi$ according to Phillips [1]
B (cm^{-1})	0.5473	$B_d = 0.5118$	0.5120
D (cm^{-1})	0.62×10^{-6}	0.70×10^{-6}	0.63×10^{-6}
q (cm^{-1})		0.00016	0.00016
r (cm)	1.602×10^{-8}	1.657×10^{-8}	1.657×10^{-8}

Table 4.

Electronic state	$a^1\Delta$	$d^1\Sigma$	$b^1\Pi$	$c^1\Phi$
$T_e + \frac{1}{2}\omega_e$ (cm^{-1})	a	$a + 2218.77$	$a + 11272.77$	$a + 17840.60$

state in common. As Phillips [1] has convincingly shown that the 8860 A-band is a Π–Δ transition, it is certain that the 11032 A-band is a Π–Σ, not a Σ–Π. The 8860 A-band is regarded as a singlet transition. The 11032 A-band is much stronger than other bands in this region. From this it follows that the 11032 A-band must be the 0-0 band of a $^1\Pi$–$^1\Sigma$ transition.

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